

IN THE ABSTRACT:

Please add the attached Abstract of the Disclosure to the specification.

REMARKS

Claims 1 through 7 have been cancelled and replaced with claims 8-17 drafted in proper U.S. format. Proper headings according to the guidelines for drafting a nonprovisional patent application under 35 U.S.C. 111(a) have been added. A proper Abstract of the Disclosure has been added to the specification.

In view of the foregoing, it is submitted that this application is now in condition for allowance and such allowance is respectfully solicited.

Authorization is herewith given to charge any fees or any shortages in any fees required during prosecution of this application and not paid by other means to Patent and Trademark Office deposit account 50-1199.

Respectfully submitted on July 12, 2001

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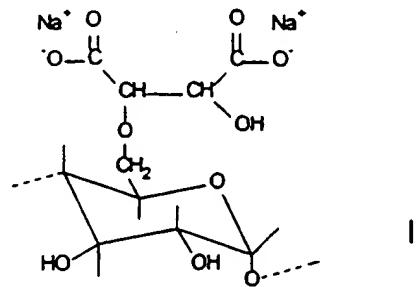
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GEH/Encl.: pages 1, 2, 8 (clean copies and marked-up versions); claims 8-17; Abstract of the Disclosure

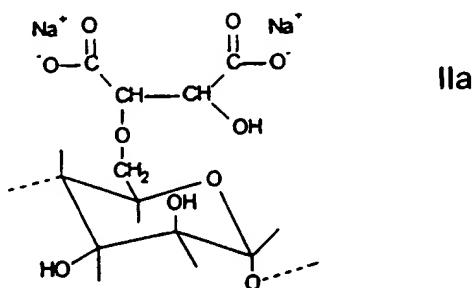
COPY OF NEW CLAIMS 8-17

8. Malatyl polysaccharides prepared by reacting polysaccharides and an epoxy compound selected from the group consisting of cis-epoxy succinate or epoxy carboxylic acids.

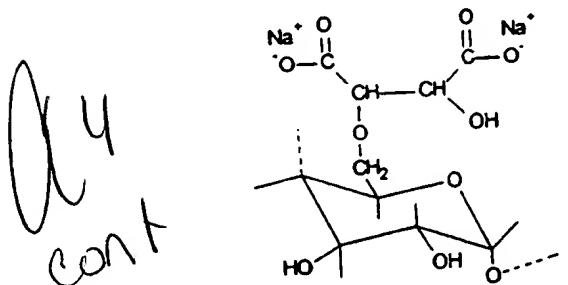
9. A malatyl polysaccharide according to claim 8 in the form of malatyl starch of the general formula (I):



10. A malatyl polysaccharide according to claim 8 in the form of malatyl galactomannan of the general formula (IIa)

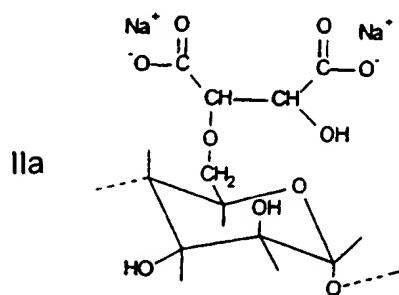


11. A malatyl polysaccharide according to claim 8 in the form of malatyl galactomannan of the general formula (IIb)

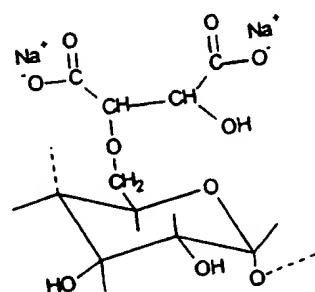


IIb

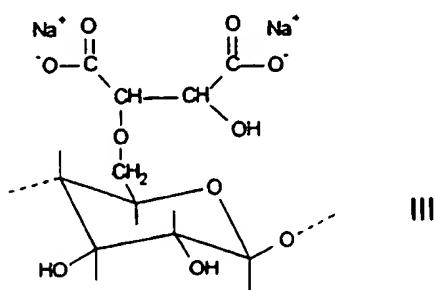
12. A malatyl polysaccharide according to claim 8 in the form of malatyl galactomannan of the general formula (IIa) and (IIb)



and



13. A malatyl polysaccharide according to claim 8 in the form of malatyl cellulose of the general formula (III).



14. A method of preparing malatyl polysaccharides according to claim 1,

comprising the step of:

reacting polysaccharides with an epoxy compound selected from the group consisting of cis-epoxy succinate or analog epoxy carboxylic acids.

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cont*

15. A method according to claim 14, wherein the epoxy compound is epoxy succinate and the step of reacting is carried out in a suspension.
16. A method according to claim 14, wherein the epoxy compound is epoxy succinate and the step of reacting is carried out in solid phase.

17. A method of using malatyl polysaccharides according to claim 8 as thickening agents or complexing agents for cations or organic compounds or as ion exchangers for aqueous systems or as adjuvants in pharmaceutical applications or as ingredients for hygiene articles.

7/12/01: Prel. Amd for Docket No. 06-01US (PCT/DE00/00065 - Int. Filing Date: 1/7/2000) Inventor(s): Lazik

## Malatyl Polysaccharides, Their Production and Their Use

### Background of the Invention

#### 1. Field of the Invention

The invention relates to malatyl polysaccharides made of polysaccharides and cis-epoxy succinate or other epoxy carboxylic acids, methods for their production as well as their use in detergents, thickening agents, complexing agents for cations or organic compounds or as ion exchangers for aqueous system or as adjuvants in pharmaceutical applications (for example, tablet bursting agents, suspension stabilizes etc.) or as ingredients in hygiene articles and medical fields.

#### 2. Description of the Related Art

In general, reactions of starch or cellulose with epoxides (oxiranes), for example, with ethylene oxide or propylene oxide, to form hydroxyalkyl derivatives have been known for quite some time and have been described in many publications (for example, K. Engelskirchen in "Methoden der organischen Chemie", Vol. E20, p. 2135ff, 1987). Hydroxyalkyl starches or hydroxyalkyl cellulose compounds are non-ionic derivatives which are used often in electrolyte-rich systems, for example, as thickening agents because they react substantially inert in aqueous systems (for example, without viscosity loss) in regard to electrolytes (salts).

Reactions of starch or cellulose to ionic derivatives have also been described often (see, *inter alia*, R. L. Davidson, *Handbook of Water-soluble Gums and Resins*, Chapter 22, 1980). The ionic derivatives have the advantage that they are soluble in cold water and thus cover a large range of applications. Carboxymethyl derivatives (for example, carboxymethyl starch or carboxymethyl cellulose) and oxidized polysaccharides are the best known representatives of ionic derivatives. These derivatives have only one ionic group (carboxyl group) per substituent and are not suitable in an advantageous manner, for example, as co-builders in detergents or water softening agents. In addition, esters of adipic acid (adipate), succinic acid (succinate) or maleic acid are common which result from esterification of the dicarboxylic acid with the glucose of the starch or cellulose. However, in this

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reaction one of the functional groups of the two carboxylic groups is lost. This is of great disadvantage when this derivative is to be used as a complexing agent for polyvalent ions (for example, calcium). For example, this complexing property would be advantageous in regard to water softening agents.

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A derivative produced from maleic acid anhydride and starch (or cellulose) in a Michael addition in alkaline medium would not lose this advantage. In this reaction, a hydroxy group of the glucose reacts with a double bond of the maleic acid with formation of an ether and with conservation of the two functional carboxyl groups. In this reaction a succinic acid ether of the starch is formed (a succinyl starch, not starch succinate, the latter would be a succinic acid ester). The disadvantage in this connection is that the yields of the maleic acid are minimal (conventionally less than 10 %) and the achievable substitution rate is small. Accordingly, it is not economical and not sufficiently efficient in its effects. Additions to a double bond with glucose or other carbohydrates are generally not efficient. Moreover, the maleic acid anhydride reacts with the starch to maleic acid ester (starch maleate) in this Michael reaction under alkaline conditions, so that in this reaction also one of the two carboxyl groups is lost as an ionic group (see R. L. Davidson, "Handbook of Water-soluble Gums and Resins", Chapter 22, pp. 22-40, 1980).

Summary of the Invention

In particular in connection with the natural base of polysaccharides there is still a high need in regard to polysaccharide derivatives with multi-functional properties. The object of the invention resides therefore in the provision of polysaccharide derivatives in which both carboxyl groups are preserved.

Surprisingly, new malatyl polysaccharides were found which can be prepared from polysaccharides and *cis*-epoxy succinate or other epoxy carboxylic acids, wherein the carboxyl groups are maintained in their preparation. However, it is also possible to use the derivatives of polysaccharides instead of native polysaccharides. This

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hygiene articles or in the medical field. For a very great degree of crosslinking, they can swell only minimally and can be used, for example, as ion exchangers for aqueous system or as additives in pharmaceutical applications (for example, tablet bursting agents, suspension stabilizers etc.).

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Description of Preferred Embodiments

In the following, embodiments of the invention will be explained in more detail.

Example 1

Malatyl Starch from Potato Starch and Disodium Epoxy Succinate made from Maleic Acid

Step 1A

Maleic acid reacts very quickly and completely with  $H_2O_2$  and 2 mol-% of a catalyst in only 1.5 hours at 65 °C to disodium epoxy succinate in almost quantitative yield: maleic acid +  $H_2O_2$  + NaOH + sodium tungstate ( $Na_2WO_4 \cdot 2H_2O$ ).

Into a one-liter round flask with stirrer, thermometer, and dropping funnel, a solution of 116 g (1.0 mole) maleic acid in 300 ml water is introduced. To this solution a solution of 60 g (1.5 mole) NaOH in 100 ml water is added. As a result of the released neutralization heat, the temperature rises to approximately 70 °C. To the hot solution 6.6 g (0.02 mole) of sodium tungstate are added.

A pH electrode is immersed into the solution and 1.2 mole of a 30-%  $H_2O_2$  (123 ml or 136 g; for 35-%  $H_2O_2$  it is 103 ml or 117 g) are added. The exothermic reaction is maintained for 15 minutes with a water bath at 65 °C, and the pH value drops from approximately 5.5 to 4. With dropwise addition of a solution of 0.5 mole (20 g) NaOH in 100 ml water the reaction solution is then maintained at a minimum of pH 4. After 1-1.5 hours of stirring at approximately 65 °C, the solution is cooled to

## MARKED-UP VERSION OF PAGE 1

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